SYNTHESIS OF PLANT GROWTH REGULATOR ANALOGUES FROM ALEURITIC ACID

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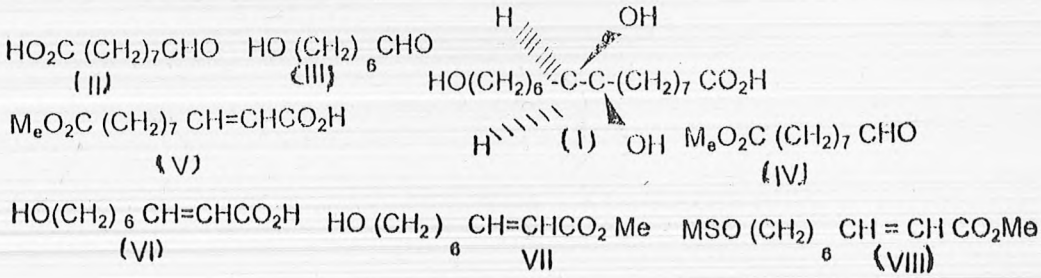
Plant growth regulators (PGR'S) having either stimulating or retarding activity are non-pollutive and cost-effective compounds to bring about changes of desired productivity in agricultural crops. Among these compounds one group comprises of the aliphatic nature[1a-f] with remarkable and definite activity in the physiology of plant growth. This paper covers syntheses of two unreported PGR analogues (VIII) and (V) from threo-aleuritic acid[2], 9, 10, 16-trihydroxyhexadecanoic acid (I), the major constituent acid of lac, believed to be present to the extent of ~35%.

(I), On periodate oxidation[3] gave quantitative yields of 7-hydroxy heptanal (III) and 9-oxononanoic acid (II). The latter on condensation with malonic acid in presence of pyridine on steam-bath for 8 hr gave 9-hydroxy -2- nonenoic acid (VI) which on esterification with MeOH – H^+ followed by mesylation yielded methyl 9-methylsulphonyloxy-2-nonenoate (VIII). Similarly II was converted into its methyl ester (IV) with diazomethane, which on condensation with malonic acid in the presence of pyridine gave 10-carboxy methyl-2-decenoic acid (V). The molecular ion peaks of V and VIII at 228 and 264 m/z confirmed the formation of the products. ^{1}HNMR spectrum of V and VIII showed doublets at δ5.83 (J=16HZ) for ethylenic proton adjacent to carboxyl group and a multiplet at δ 5.54 for ethylenic proton attached to chain methylene groups.



EXPERIMENTAL AND DISCUSSION

IR spectra were recorded on a Perkin-Elmer 237 spectrophotometer. Mass spectra on Jeol D-300 (Ei/ci) spectrometer with retention time 0.44 and 2.5. ^{1}HNMR spectra (chemical shifts in δ ppm) on FTNMR instrument using TMS as internal standard. All the solvents were freshly distilled. Compounds were routinely checked by tlc.

9-Oxononanoic acid (II) : (I) (30.4g, 100 m mol) was added to aq. Na_2CO_3 solution (5.8%,110ml)with slight warming. After dissolution of (I), the solution was filtered and the filtrate

was acidified with H_3PO_4 (10%) till tutibidility appeared (pH ca 7). $CHCl_3$ (200 ml) was then added, the mixture was warmed to 30° when aq. $NaIO_4$ (22g, 200 ml) was added over a period of 30 min. After stirring for 15 min., the mixture was cooled (5—10°), acidified to pH 3 with H_3PO_4 (20%~35 ml) and filtered. The organic layer was separated and extracted thoroughly with saturated $NaHCO_3$ solution (2×50 ml) followed by aq. Na_2CO_3 solution (5%, 50 ml). The organic layer was then washed with water, brine and dried (Na_2SO_4). The combined aq. portions was acidified with H_3PO_4 (10%) to pH 3 and extracted with $CHCl_3$. Which on usual workup gave (II) (17g) as a thick liquid, ν max 1728, 1700 cm^{-1} ; $\delta(CDCl_3)$ 1. 11-1. 82 (10 H, *m*, CH_2COOH), 2.3 (4H, *t*, CH_2CHO), 9.55 (1H, *t*, CHO), 9.87 (1H, *bs*, COOH).

7-Hydroxyheptanal (III) : (III) (12g) was recovered from $CHCl_3$ layer initially obtained under vacuum as liquid, νmax 3250, 1720 cm^{-1} ; $\delta(CDCl_3)$ 2.46(2H, *m*, CH_2CHO) 2.39 (1H, *br*, CH_2OH, D_2O exchangeable), 3.72 (2H, *t*, CH_2OH), 9.91 (1H, *t*, CH_2CHO).

Methyl 9-oxononanoate (IV) : The ethereal solution of (II) was treated with fresh ethereal solution of diazomethane to obtain (IV) (yield 90%) also as an oil. $\delta(CDCl_3)$ 1.0-1.88 (10H, *m*, 5-CH_2), 1.94-2.52(4H, *m*, CH_2COOCH_3 and CH_2CHO), 3.62(3H, *s*, $COOCH_3$) 8.70 (1H, *t*, CHO).

10-carboxymethyl 2-decenoic acid (*V*) :

(IV) (5.8 g, 31.2 m mol) in dry pyridine (5g) was added dropwise to malonic acid (6.5 g, 62.5 m mol) in dry pyridine (8.7 g) and stirred for 10 min. The content was shaken for another 10-15 min and heated on steam-bath for 8 hrs till the evolution of CO_2 ceased. The reaction mixture was poured into water (25 ml) and the solution extracted with ether (2×200 ml). The ethereal solution was washed with dil HCl (25%), water and dried (Na_2SO_4). The ethereal solution was concentrated and eluted through a silicagel column with hexane—EtOAc (93:7). The pure (V) was recovered as viscus liquid (3.47g), 48.8%. $\delta(CDCl_3)$: 5.83 (IH, *d*, $-CH=CHCO_2H$, J=16HZ), 5.54 (1H, *m*, $CH-CHCO_2H$, 3.66 (3H, *s*—CH_3OCO), 2.32 (2H, *t*, CH_2OCOCH_3 ; J=8HZ), 2.23(2H, *q*—$CH_2-CH=CH$), 1.33—1.62 (10H, *br*, $(CH_2)n$), MS (m/z) 228(M^+0.7).

Methyl 9-hydroxy-2-nonenoate (VII) : 9-Hydroxy-2-nonenoic acid (VI) (4.36 g, 71.5%) was obtained from III (4.6 g, 35.4 m mol) by adopting the same procedure as for (IV). (VI) (3.1g, 18m mol) was esterified with dry MeOH. BF_3. Et_2O complex (51 ml) by refluxing for 15 min. Usual work-up afforded the title compound (VII) (.34g, 40%) as a liquid showing single spot on tlc (Hexane, EtOAc—1 : 1).

Methyl 9-methylsulphonyloxy-2-nonenoate (VIII) : (VII) (1.2g, 6.5 m mol) NEt_3 (0.98g, 9.8 m mol) and CH_2Cl_2 (15 ml) were well mixed and cooled to O°. Mesylchloride (0.8186g, 7.15 m mol) was added drop wise to the cooled reaction mixture during 30 min. The reaction mixture was transferred to a separating funnel with additional 10 ml of CH_2Cl_2 and washed with ice-water, cold HCl (10%), saturated $NaHCO_3$ soln. and brine sequentially,

dried (Na_2SO_4). Removal of the solvent furnished VIII as a liquid (1.42g, 83%) showing single spot on tlc (Hexane, EtOAc—10 : 3).

$\delta(CDCl_3)$: 5.84 (IH, d, $-CH=CH-CO_2H$, J = 16 HZ), 5.54(IH, *br*, $-CH=CH-CO_2H$),4.23 (2H, *t*, $-CH_2-OSO_2\ CH_3$, J = 6HZ), 3.74 (3H, *s*, $-COOCH_3$), 3.02(3H, *s*, $-CH_3\ SO_2O$), 2.34 (2H, *t*, $-CH_2-OSO_2CH_3$), 2.22 (2H, *q*, $-CH_2-CH=CH-$), 1.38 – 1.8(10H, *m*, $-(CH_2)n$) ; MS (m/z) : 264(M^+, 0.9), 233($M-OCH_3$, 9.9), 205($M-CO_2CH_3$, 0.4), 185 ($M-SO_2CH_3$, 2.6).

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SUMMARY

Plant glowth regulator analogues, methyl 9-methylsulphonyloxy-2 nonenoate (VIII) and 10-carboxymethyl 2-decenoic acid (V) were synthesised from 7-hydroxyheptanal (III) and 9-oxononanoic acid (II), the periodate oxidation products of *threo*--aleuritic acid (I), the major constituent acid of lac (~35%) adopting simple reaction sequences. The products were ^{1}HNMR and mass spectra.

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